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(54) A method for the manufacture of yellow azo-based pigments

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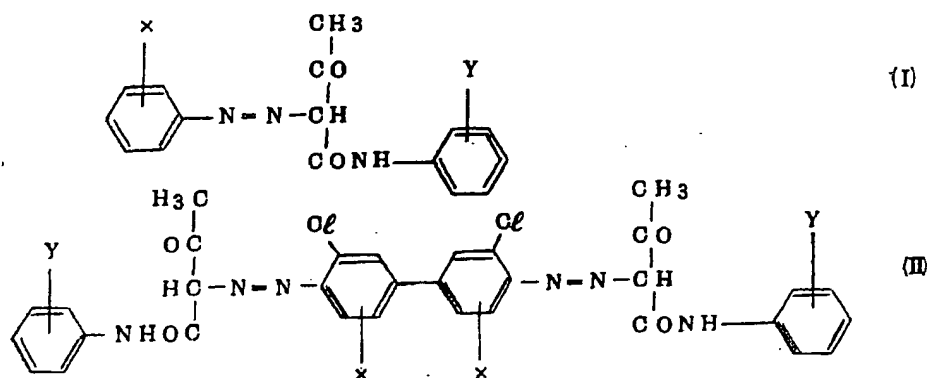
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### Scope of the Patent Claim

A method for the manufacture of yellow azo-based pigments, characterized in that alkaline earth metal salts or organic amine salts of a sulphonic acid of pigment (I) or pigment (II), which can be represented by the general formulae indicated below, are mixed with pigment (I) or pigment (II) or a mixture of these pigments.



(X and Y in these formulae signify one or more substituent groups selected from among the group comprising H, CH<sub>3</sub>, Cl, NO<sub>2</sub> and OCH<sub>3</sub>.)

### Detailed Description of the Invention

The invention concerns a method for the manufacture of yellow azo-based pigments which can be dispersed in a low viscosity non-aqueous vehicle and provide dispersions which have excellent fluidity.

Dispersions of the Fast Yellow-based pigments which can be represented by general formula (I) indicated below and the Benzidine Yellow-based pigments which can be represented by general formula (II) indicated below in a low-viscosity non-aqueous vehicle, such as paints and gravure inks and the like for example, sometimes exhibit a high viscosity, and there are cases where gelling occurs during prolonged storage and the materials become difficult to use.

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(X and Y in these formulae signify one or more substituent groups selected from among the group comprising H, CH<sub>3</sub>, Cl, NO<sub>2</sub> and OCH<sub>3</sub>.)

The inventors have already recognized that the admixture of the sulphonic acid organic amine salts or sulphonic acid alkaline earth metal salts of the copper phthalocyanine-based pigments with copper

phthalocyanine-based pigments is very effective for preventing a rise in viscosity during storage of non-aqueous vehicle dispersions of copper phthalocyanine-based pigments (Japanese Examined Patent Publications S39-28884 and S40-4143). The present invention is an extension of this technology and provides a method for the manufacture of yellow azo-based pigments which have excellent fluidity as low viscosity non-aqueous vehicle dispersions of the abovementioned yellow azo-based pigments (I) and (II) with acetoacetoanilide as coupler, and with which there is virtually no rise in viscosity even on prolonged storage.

Thus, the present invention involves the admixture of a sulphonic acid alkaline earth metal salt or organic amine salt of a pigment which can be represented by general formula (I) or general formula (II), or a mixture of both (I) and (II). More precisely, it involves the admixture of a sulphonic acid alkaline earth metal salt or sulphonic acid amine salt of the azo-based pigment (I) or (II) with the Pigments, or carrying out coupling by mixing a diazo

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component or coupler which has a sulpho group  $-SO_3H$  as an intermediate of (I) or (II), which is to say in the diazo component or the coupler, and forming a lake of the dye with an alkaline earth metal salt or an organic amine.

If the amount of intermediate to which a sulpho group is bonded or pigment which has a sulphonic acid salt group which is admixed is too small then the effect of improving the fluidity of the dispersion is slight, and if the amount is too great then the alkali-resistance of the film which is produced is adversely affected, and so a suitable amount should be determined for each individual case, but in general the amount of pigment which has sulphonic acid salt groups is best selected within the range from 5 to 20 wt% with respect to the whole of the pigment. Furthermore, it is possible to control the hue, light resistance and solvent resistance of the target pigment by means of different combinations of the type of intermediate which has a sulpho group or pigment which has sulphonic acid salt group and different types of intermediate which do not have a sulpho group or pigment which does not have sulphonic acid salt groups. In this case as well the fluidity is improved in the same way, and illustrative examples are described below.

### Example 1

3,3'-Dichlorobenzidine hydrochloric salt (58.7 g, 0.18 mol) was added to 200 cc of hot water and then 75 g (0.72 mol) of 35% hydrochloric acid were added and a solution was obtained, ice-water was added (liquid volume 2500 cc) and, while maintaining the liquid at a temperature of 0°C, 62 g of a 40% sodium nitrite aqueous solution (0.36 mol) were added and tetrazotization was achieved. Then 4 g of active carbon were added to decolorize the solution, the mixture was filtered, the excess nitrous acid was removed with sulphamic acid and tetrazotized solution (I) was obtained.

On the other hand, 2 g of sodium carbonate were dissolved in 200 cc of water at 50°C, 7.5 g (0.04 mol) of p-toluidine-m-sulphonic acid were added and dissolved and then 10.4 g (0.1 mol) of 35% hydrochloric acid were added and the p-toluidine-m-sulphonic acid was precipitated out. Ice-water was added to this (liquid volume 400 cc) and 6.9 g of 40% sodium nitrite aqueous solution (0.04 mol) was added while maintaining a liquid temperature of 5°C and diazotization was carried out, and the excess nitrous acid was removed with sulphamic acid and diazotized liquid (II) was obtained.

Separately, 48 g (1.2 mol) of caustic soda was dissolved in 2 l of water, 78 g (0.44 mol) of acetoacetoanilide were dissolved in the resulting solution, 80 g of 90% acetic acid were then added and ice-water was added to adjust the liquid temperature to 20°C and the liquid volume to 3 l, and a coupler solution was obtained. The abovementioned diazotized liquid (II) was added to this solution at from 5 to 10°C and coupling was carried out, and then the tetrazotized liquid (I) was added at from 0 to 5°C and coupling was carried out. After stirring the mixture for about 1 hour, the mixture was filtered and the precipitate was redispersed in 5 l of water, sodium carbonate was added and the pH was adjusted to from 8.0 to 8.5, and then 60 g of 10% barium chloride aqueous solution were added and, after heating to 80°C, the pigment was filtered off, washed with water and dried. Recovery 130 g.

Separately, for comparison, coupling was carried out in the conventional way with acetoacetoanilide and just the tetrazotized liquid (I) in the same way as described above, and a pigment with no sulphonic acid salt

group was obtained.

The two pigments prepared in this way were each dispersed using a ball mill in a lime rosin-toluene based vehicle (solid fraction 55%) and the viscosity (BM type rotation viscometer, 25°C) of the dispersion (pigment fraction 7%) with the pigment which contained the sulphonic acid salt groups was found to be considerably lower than that of the conventional product which did not contain sulphonic acid salt groups, as indicated below. Moreover, virtually no change in viscosity from the initial viscosity was seen when the pigment dispersion had been stored for 3 months.

Rate of Rotation	Pigment of the Invention		Conventional Product	
	When Prepared	After 3 Months	When Prepared	After 3 Months
6 r.p.m.	650 c.p.s.	800 c.p.s.	5240 c.p.s.	6560 c.p.s.
12	387	550	2810	3820
30	225	320	1340	2650
60	158	250	722	2200

### Example 2

A tetrazotized liquid (I) of 55.5 g (0.17 mol) of 3,3'-dichlorobenzidine hydrochloric acid salt was prepared in the same way as in Example 1. On the other hand, a coupler solution was prepared in the same way as in Example 1 by adjusting an acetic acid solution of 65.5 g (0.37 mol) of acetoacetanilide to a liquid temperature of 20°C and a liquid volume of 2 l. The tetrazotized liquid (I) was added to the coupler solution at from 0 to 5°C, coupling was carried out and a pigment slurry (II) was obtained. Separately, 3 g of sodium carbonate were dissolved in 300 cc of water at 60°C, 13.3 g (0.06 mol) of C-Acid (2-amino-4-methyl-5-chlorobenzenesulphonic acid) were dissolved in this solution and then 18.8 g (0.18 mol) of 35% hydrochloric acid were added and the C-Acid was precipitated out. Ice-water was added, the liquid temperature was set to 5°C and the liquid volume was set to 500 cc, 10.3 g (0.06 mol) of 40% sodium nitrite aqueous solution were added while maintaining the same temperature and diazotization was carried out, the excess nitrous acid was removed with sulphamic acid and diazotized liquid

(III) was obtained. Separately again, 6 g of caustic soda were dissolved in 300 cc of water, 12.6 g (0.066 mol) of acetoaceto-o-toluidide were dissolved in this solution, 10 g of 90% acetic acid were added and the toluidide was precipitated out, and the liquid temperature was adjusted to 25°C and the liquid volume was adjusted to 600 cc. The abovementioned diazotized liquid (III) was added to this liquid and, after coupling, the precipitate was filtered off and redispersed in 1.5 l of water and, after adjusting to pH from 8.0 to 8.5 with sodium carbonate, it was heated to 50°C, a solution obtained by dissolving 15 g of the acetic acid salt of palmitylamine in 100 cc of water was added and a lake was formed, and this was pigment lake (IV). This was added to the abovementioned pigment slurry (II), filtered off and dried. Recovery 132 g.

Separately, for comparison, coupling was carried out in the conventional way with acetoacetoanilide and just the tetrazotized liquid (I) in the same way as described above, and a pigment with no sulphonic acid salt groups was obtained.

These two pigments were each dispersed using a ball mill in a nitrocellulose-based vehicle (solid fraction 17%) and the viscosity (BM type rotation viscometer, 24°C) of the dispersion (pigment fraction 5.5%) which contained sulphonic acid salt groups was found to be considerably lower than that of the conventional product which did not contain sulphonic acid salt groups as indicated below. Moreover, virtually no change in viscosity from the initial viscosity was seen when the pigment dispersion had been stored for 3 months.

Rate of Rotation	Pigment of the Invention		Conventional Product	
	When Prepared	After 3 Months	When Prepared	After 3 Months
6 r.p.m. 12	1580 c.p.s. 982	1780 c.p.s. 1130	4300 c.p.s. 2380	6200 c.p.s. 4300
30 r.p.m. 60	500 c.p.s. 338	620 c.p.s. 450	1160 c.p.s. 686	3200 c.p.s. 2560

### Example 3

A tetrazotized liquid (I) was obtained in the same way as in Example 1

by tetrazotizing 65.2 g (0.2 mol) of 3,3'-dichlorobenzidine hydrochloric acid salt and adjusting the liquid volume to 2.8 l and the liquid temperature to from 0 to 5°C. Separately, 40 g of caustic soda were dissolved in 2 l of water at 25 °C, 11.8 g (0.04 mol) of acetoacetosulphonic acid anilide potassium salt and 65.5 g (0.37 mol) of acetoacetoanilide were dissolved in this solution, 72 g of 90% acetic acid were added and the acetoacetoanilide was precipitated out, and the liquid volume was set to 2.8 l and the liquid temperature was set to 20 °C. The abovementioned tetrazotized liquid (I) was added to this and coupling was carried out and, after filtration, the precipitate was redispersed in 5 l of water, sodium carbonate was added to set the pH to from 8.0 to 8.5, and the dispersion was heated to 60°C and 40 g of a 10% calcium chloride aqueous solution were added to form a lake and, after stirring for 10 minutes, this was filtered off and dried. Recovery 128.5 g.

The pigment obtained in this way was dispersed with a ball mill in a lime rosin-toluene based vehicle (solid fraction 55%) in the same way as in Example 1 and the viscosity (BM type rotation viscometer, 25°C) of the dispersion (pigment fraction 7%) was found to be considerably lower than that of the conventional product indicated in Example 1 as indicated below. Moreover, virtually no change in viscosity from the initial viscosity was seen when the pigment dispersion had been stored for 3 months.

Rate of Rotation	When Prepared	After 3 Months
6 r.p.m.	430 c.p.s.	490 c.p.s.
12	400	450
30	370	410
60	350	390

#### Example 4

3,3'-dichlorobenzidine hydrochloric acid salt 9.8 g (0.03 mol) was tetrazotized in the same way as in Example 1 to prepare tetrazotized liquid (I). Separately, 19.5 g (0.066 mol) of acetoaceto-p-sulphonic acid anilide potassium salt was reprecipitated and a coupler liquid was obtained in the same way as in Example 3. Tetrazotized liquid (I) was added to this and coupling was carried out, the material was filtered off and washed with water



and then redispersed in 1.5 l of water, the pH was adjusted to from 8.0 to 8.5 with sodium carbonate and 60 g of 10% calcium chloride aqueous solution were added, while heating to 60°C, and a lake was formed, and this was taken as pigment slurry (II).

Separately, 3,3'-dichlorobenzidine was tetrazotized with sodium nitrite in the usual way and coupled with acetoaceto-o-toluidide in sodium acetate buffer solution to prepare pigment slurry (III). The abovementioned pigment slurry (II) (pigment content 34 g) was added to pigment slurry (III) (pigment content 300 g) and, after stirring, the pigment was filtered off and dried. Recovery 334 g.

When this pigment was dispersed in a lime rosin-toluene based vehicle (solid fraction 55%) in a ball mill, the viscosity of the dispersion (pigment fraction 7%) (BM type rotation viscometer, 25°C) was very low when compared with that of the conventional product indicated in Example 1, as indicated below. The viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

Rate of Rotation	When Prepared	After 3 Months
6 r.p.m.	700 c.p.s.	800 c.p.s.
12	415	500
30	270	360
60	178	250

### Example 5

35% hydrochloric acid 10.5 g (1.0 mol) was added to 58.7 g (0.34 mol) of 4-chloro-2-nitroaniline, ice-water was added and the liquid temperature was set to 0°C and the liquid volume was set to 2 l. A 40% sodium nitrite solution 58.6 g (0.34 mol) at the same temperature was added and diazotization was carried out, 7 g of active carbon were added and the mixture was decolorized and then filtered and the excess nitrous acid was removed with sulphamic acid and diazotized liquid (I) was obtained.

Separately, 65.5 g (0.37 mol) of acetoacetoanilide were added to 2 l of water at 25°C and dissolved, 61.2 g of 90% acetic acid were added and the material was reprecipitated, the liquid volume was adjusted to 2.5 l and the

liquid temperature was adjusted to 15°C and a coupler liquid was obtained.

The abovementioned diazotized liquid (I) was added to this coupler liquid and coupling was carried out, and pigment slurry (II) was obtained. Recovery 120 g. A slurry corresponding to 10 g of the pigment lake (IV) which was the palmitylamine salt of the coupling product of C-Acid and acetoaceto-o-toluidide indicated in Example 2 was added to the pigment slurry (II) obtained in this way and, after stirring, the pigment was filtered off and dried. Recovery 130 g.

Separately, for comparison, acetoacetoanilide was coupled with 4-chloro-2-nitroaniline in the usual way and a pigment which had no sulphonic acid salt groups was obtained.

When these two pigments were dispersed in a nitrocellulose-based vehicle based vehicle (solid fraction 17%) in a ball mill the viscosities (BM type rotation viscometer, 25°C) of the dispersions (pigment fractions 5.5%) were such that the viscosity of the pigment which contained sulphonic acid salt groups was very low when compared with that of the conventional product which did not have sulphonic acid salt groups, as indicated below. Moreover, the viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

Rate of Rotation	Pigment of the Invention		Conventional Product	
	When Prepared	After 3 Months	When Prepared	After 3 Months
6 r.p.m.	1220 c.p.s.	1320 c.p.s.	5560 c.p.s.	7200 c.p.s
12	930	1030	3120	4600
30	475	560	1360	2850
60	325	405	870	2360

### Example 6

4-Chloro-2-nitroaniline 69 g (0.4 mol) was diazotized in the same way as in Example 5 and diazotized liquid (I) was obtained.

On the other hand, 40 g of caustic soda was dissolved in 2 l of water at 25°C and then 11.8 g (0.04 mol) of the potassium salt of acetoaceto-p-sulphonic acid anilide and 65.5 g (0.37 mol) of acetoacetoanilide

were added and dissolved, and then 72 g of 90% acetic acid were added, the liquid volume was adjusted to 2.5 l, the liquid temperature was adjusted to 15°C and a coupler liquid was obtained. The abovementioned diazotized liquid (I) was added to this coupler liquid and coupled, and then the precipitate was filtered off and washed with water and then dispersed in 5 l of water, 40 g of 10% calcium chloride aqueous solution were added and a lake was formed, and the material was filtered off, washed with water and dried. Recovery 140 g.

When this pigment was dispersed in a nitrocellulose-based vehicle (solid fraction 17%) as shown in Example 5 in a ball mill the viscosity (BM type rotation viscometer, 25°C) of the dispersion (pigment fraction 5.5%) was very low when compared with that of the conventional product indicated in Example 5, as indicated below. Moreover, the viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

Rate of Rotation	When Prepared	After 3 Months
6 r.p.m.	1080 c.p.s.	1180 c.p.s.
12	970	1080
30	495	580
60	308	400

### Example 7

4-Chloro-2-nitroaniline 62.1 g (0.36 mol) was diazotized in the same way as in Example 5, the liquid volume was adjusted to 2.5 l and the liquid temperature was adjusted from 0 to 5°C, and diazotized liquid (I) was obtained.

Separately, 6.9 g (0.04 mol) of sulphanilic acid were added to 200 cc of water, 2 g of sodium carbonate were added and the sulphanilic acid was dissolved at 50°C. 35% hydrochloric acid 12.5 g (0.12 mol) and ice-water were then added and the solution volume was adjusted to 300 cc and the liquid temperature was adjusted to 5°C and 7 g of a 40% sodium nitrite solution were added at the same temperature and diazotization was carried out and then the excess nitrous acid was removed with sulphamic acid. The

liquid volume was adjusted to 400 cc and the liquid temperature was adjusted to from 0 to 10°C and diazotized liquid (II) was obtained.

Caustic soda (40 g) was dissolved in 2 l of water and then 76 g (0.43 mol) of acetoacetoanilide were added and dissolved, 72 g of 90% acetic acid were added and the anilide was precipitated and then the liquid volume was adjusted to 2.5 l and the liquid temperature was adjusted to 15°C. The abovementioned diazotized liquid (II) was added to this liquid and coupling was carried out, and then the abovementioned diazotized liquid (I) was added and coupling was carried out. The precipitate was filtered off and washed with water and then redispersed in 5 l of water, sodium carbonate was added and the pH was adjusted to from 8.0 to 8.5 and then the dispersion was heated to 85°C, 60 g of 10% calcium chloride aqueous solution were added and a lake was formed, and the material was filtered off, washed with water and dried. Recovery 137 g.

Separately, for comparison, just acetoacetoanilide was coupled with 4-chloro-2-nitroaniline in the usual way and a pigment was obtained.

When these two pigments were dispersed in a lime rosin-toluene based vehicle based vehicle (solid fraction 17%) in a ball mill the viscosities (BM type rotation viscometer, 25°C) of the dispersions (pigment fractions 7%) were such that the viscosity of the pigment which contained sulphonic acid salt groups was very low when compared with that of the conventional product which did not have sulphonic acid salt groups, as indicated below. Moreover, the viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

Rate of Rotation	Pigment of the Invention		Conventional Product	
	When Prepared	After 3 Months	When Prepared	After 3 Months
6 r.p.m.	1700 c.p.s.	1810 c.p.s.	3760 c.p.s.	5770 c.p.s
12	10800	1180	3010	5020
30	476	570	1030	3040
60	320	400	576	2180

### Example 8

A tetrazotized liquid (I) of 55.5 g (0.17 mol) of 3,3'-dichlorobenzidine hydrochloric acid salt was obtained in the same way as in Example 1. Furthermore, an acetic acid solution of 65.5 g (0.37 mol) of acetoacetoanilide was adjusted to a liquid temperature of 20°C and a liquid volume of 2 l and a coupler liquid was obtained in the same way as in Example 1. The tetrazotized liquid (I) was added to this at from 0 to 5°C and coupling was carried out, and pigment slurry (I) was obtained.

Separately, 3 g of sodium carbonate were dissolved in 300 cc of water and dissolved at 60°C, 12 g (0.06 mol) of 3-amino-4-methoxybenzenesulphonic acid were dissolved in the solution and then 18.8 g (0.18 mol) of 35% hydrochloric acid were added and the abovementioned sulphonic acid was precipitated out. Ice-water was added and the liquid temperature was set to 5°C and the liquid volume was set to 50 cc and 10.3 g (0.06 mol) of 40% sodium nitrite aqueous solution were added while maintaining the same temperature and diazotization was carried out, the excess nitrous acid was removed with sulphamic acid and diazotized liquid (III) was obtained. Furthermore, separately, 6 g of caustic soda were added to 300 cc of water and dissolved, 12.6 g (0.066 mol) of acetoaceto-o-toluidide were dissolved in the solution, 10 g of 90% acetic acid were added and the toluidide was precipitated out, and the liquid volume was adjusted to 600 cc and the liquid temperature was adjusted to 25°C. The abovementioned diazotized liquid (III) was then added to this liquid, and then the precipitate was filtered off and redispersed in 1.5 l of water and, after adjusting the pH to from 8.0 to 8.5 with sodium carbonate, the mixture was heated to 50°C and a solution obtained by dissolving 9.2 g of aniline sulphuric acid salt in 100 cc of water was added and a lake was formed, and pigment lake (IV) was obtained. This was added to the abovementioned pigment slurry (II), filtered and dried. Recovery 125 g.

When this pigment was dispersed in a nitrocellulose-based vehicle (solid fraction 17%) in a ball mill the viscosity (BM type rotation viscometer, 25 °C) of the dispersion (pigment fraction 5.5%) was very low when compared with that of the conventional product indicated in Example 2, as indicated

below. The viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

Rate of Rotation	When Prepared	After 3 Months
6 r.p.m.	1600 c.p.s.	1900 c.p.s.
12	1010	1120
30	600	700
60	420	460

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